US009156265B2

(12) United States Patent
Asada

(10) **Patent No.: US 9,156,265 B2**
(45) **Date of Patent: Oct. 13, 2015**

(54) **MANUFACTURING METHOD OF LIQUID EJECTING HEAD**

(71) Applicant: **SEIKO EPSON CORPORATION**, Tokyo (JP)

(72) Inventor: **Koji Asada**, Azumino (JP)

(73) Assignee: **Seiko Epson Corporation**, Tokyo (JP)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **14/204,583**

(22) Filed: **Mar. 11, 2014**

(65) **Prior Publication Data**

US 2014/0284305 A1 Sep. 25, 2014

(30) **Foreign Application Priority Data**

Mar. 21, 2013 (JP) 2013-058559

(51) **Int. Cl.**
B41J 2/16 (2006.01)
B41J 2/14 (2006.01)

(52) **U.S. Cl.**
CPC ***B41J 2/1607*** (2013.01); ***B41J 2/161*** (2013.01); ***B41J 2/1623*** (2013.01); ***B41J 2/1629*** (2013.01); ***B41J 2/1645*** (2013.01); ***B41J 2/1646*** (2013.01); *B41J 2002/14241* (2013.01); *B41J 2002/14419* (2013.01)

(58) **Field of Classification Search**
CPC B41J 2/1607; B41J 2/161; B41J 2/1623
USPC 216/27
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

2011/0069121 A1* 3/2011 Park et al. 347/47

FOREIGN PATENT DOCUMENTS

JP 4798348 8/2011

* cited by examiner

Primary Examiner — Nadine Norton
Assistant Examiner — Mahmoud Dahimene
(74) *Attorney, Agent, or Firm* — Workman Nydegger

(57) **ABSTRACT**

A piezoelectric actuator which is provided on the flow path formation substrate, and a protection substrate which is bonded to the flow path formation substrate on the piezoelectric actuator side, the method including: bonding the flow path formation substrate on which the piezoelectric actuator is formed, and the protection substrate to form a bonded body; bonding a sealing member to the protection substrate of the bonded body on the surface side opposite the flow path formation substrate, and disposing a protection material containing a nitro compound in a space between the sealing member and the protection substrate.

4 Claims, 6 Drawing Sheets

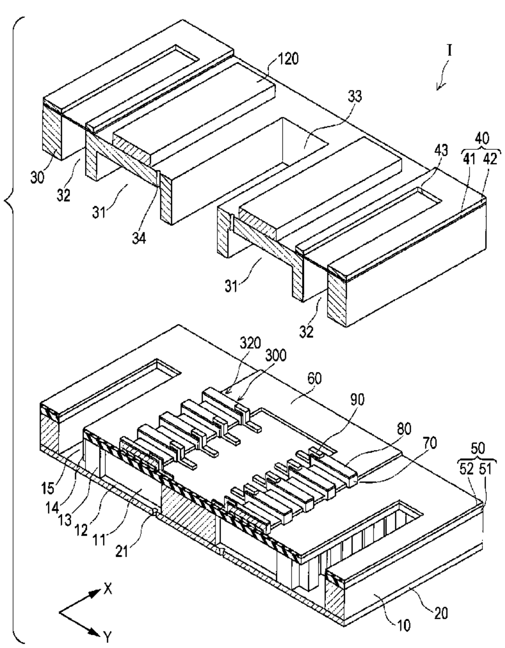
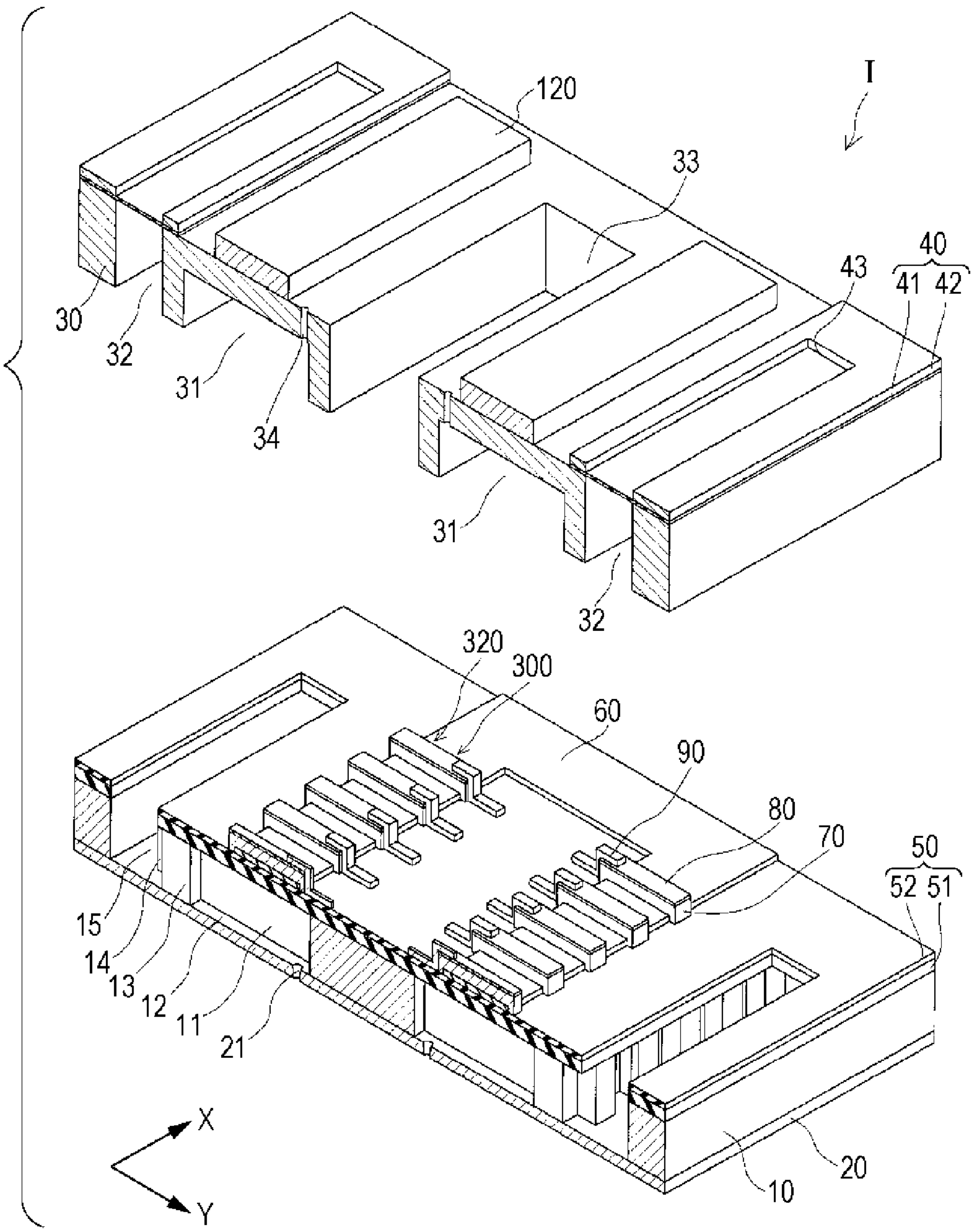
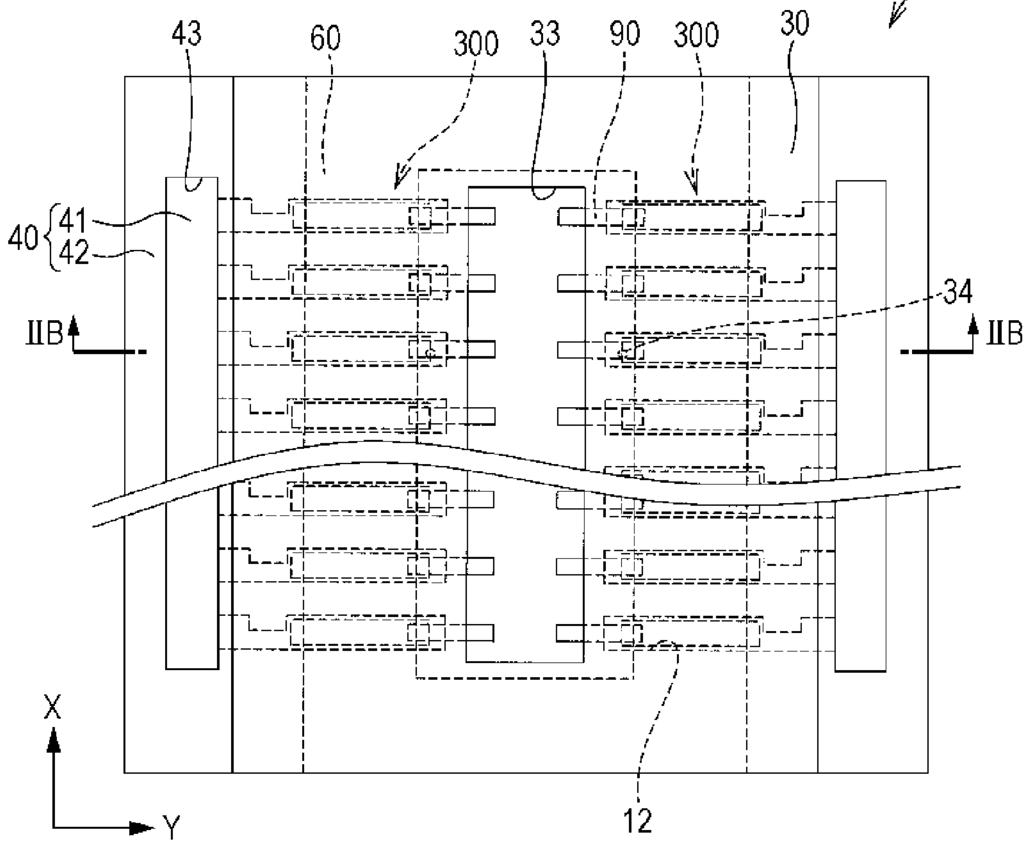


FIG. 1



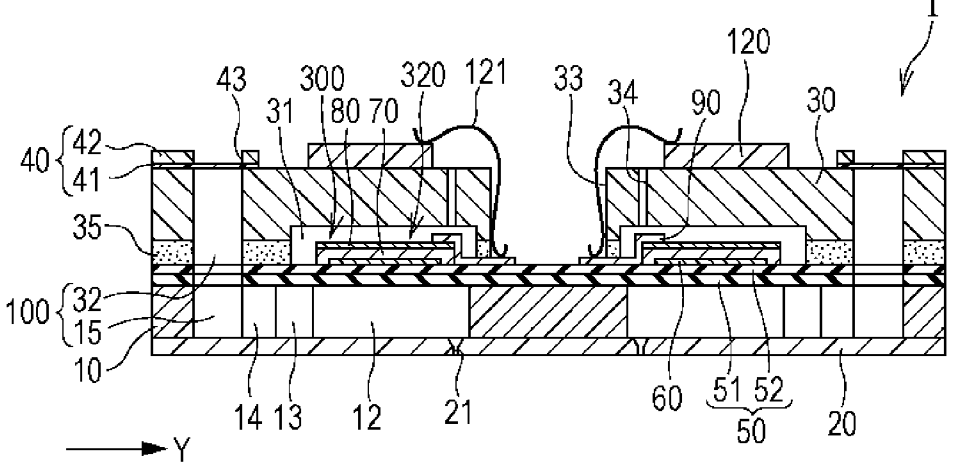
I
120
33
40
41 42
43
30
32
31
34
31
32
320
300
60
90
80
70
50
52 51
15
14
13
12
11
21
X
Y
10
20

FIG. 2A



I
43
60
300
33
90
300
30
40
41
42
IIB
IIB
34
X
Y
12

FIG. 2B



I
120
43
300
320
121
33
34
90
30
31
80
70
40
42
41
35
100
32
15
10
14
13
12
21
60
51
52
50
20
Y

FIG. 3A

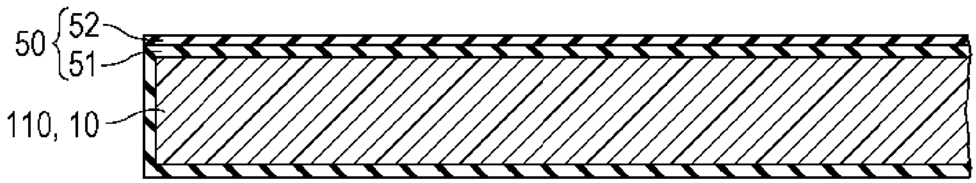


FIG. 3B

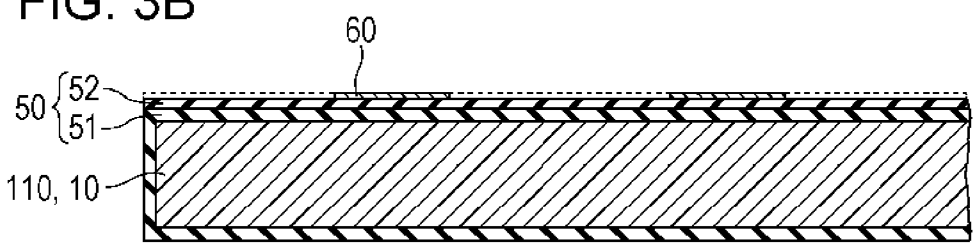


FIG. 3C

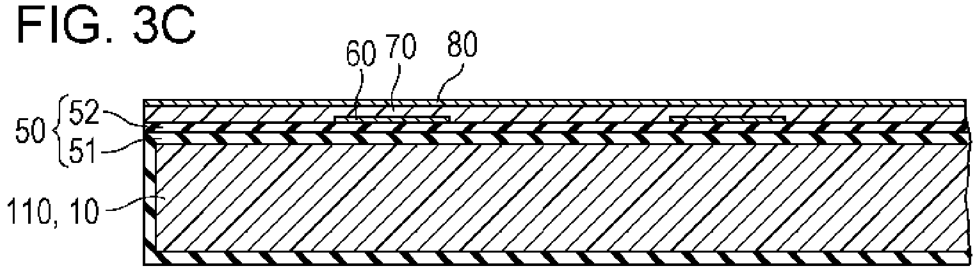


FIG. 3D

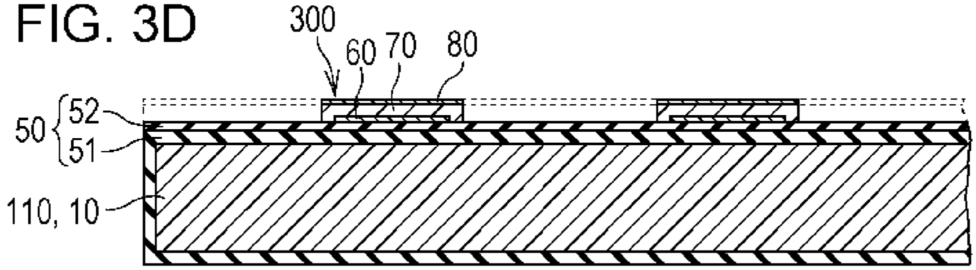


FIG. 4A

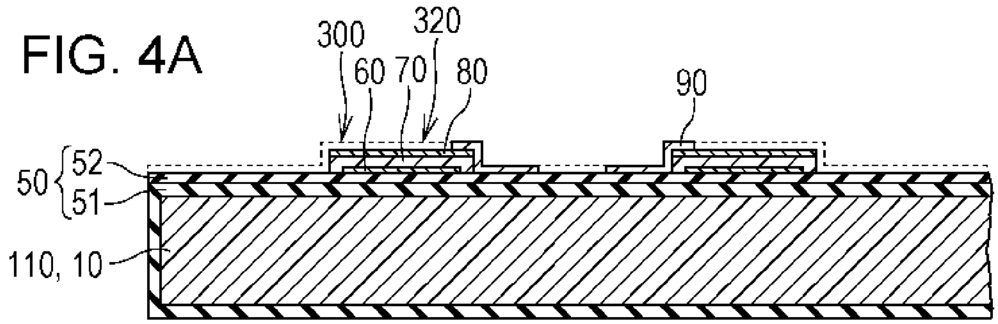


FIG. 4B

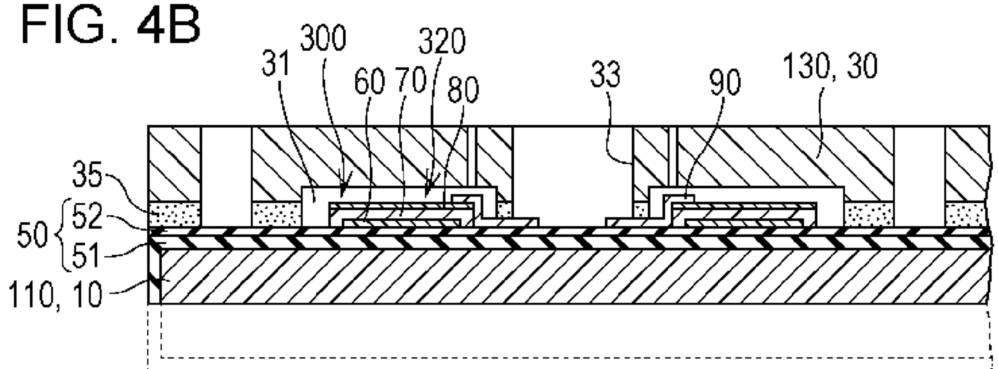


FIG. 4C

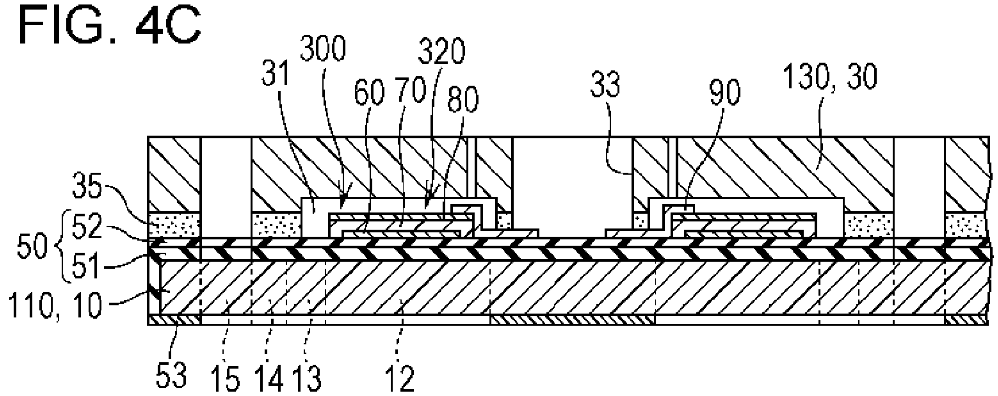


FIG. 5A

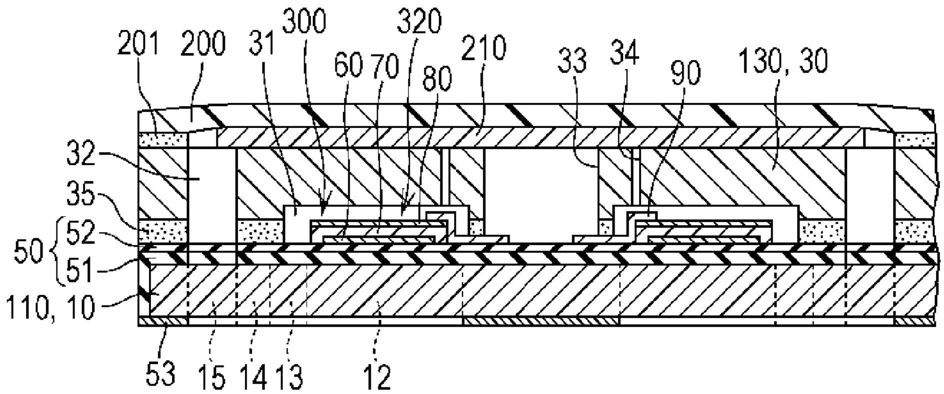

201
200
31
300
320
60
70
80
210
33
34
90
130, 30
32
35
52
50
51
110, 10
53
15
14
13
12

FIG. 5B

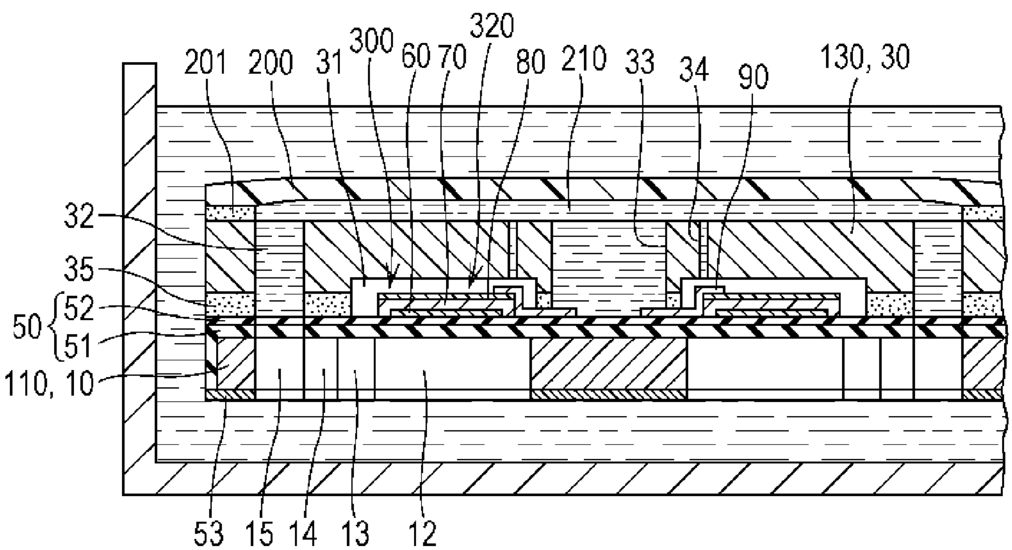

201
200
31
300
60
70
320
80
210
33
34
90
130, 30
32
35
52
50
51
110, 10
53
15
14
13
12

FIG. 6A

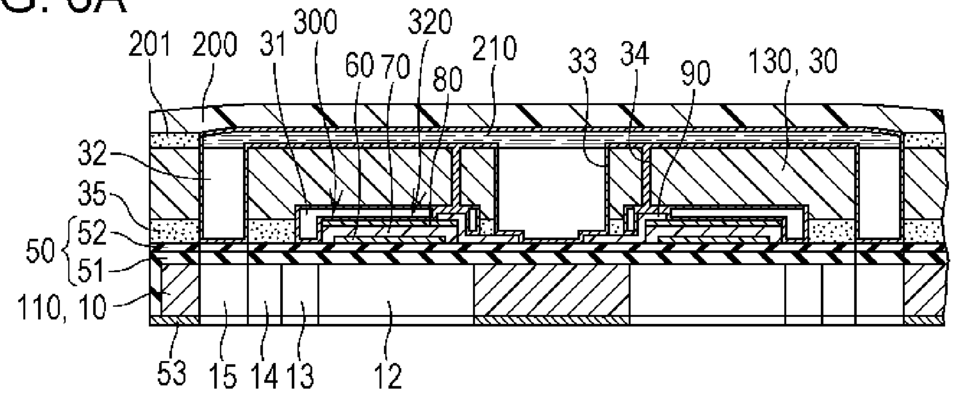


FIG. 6B

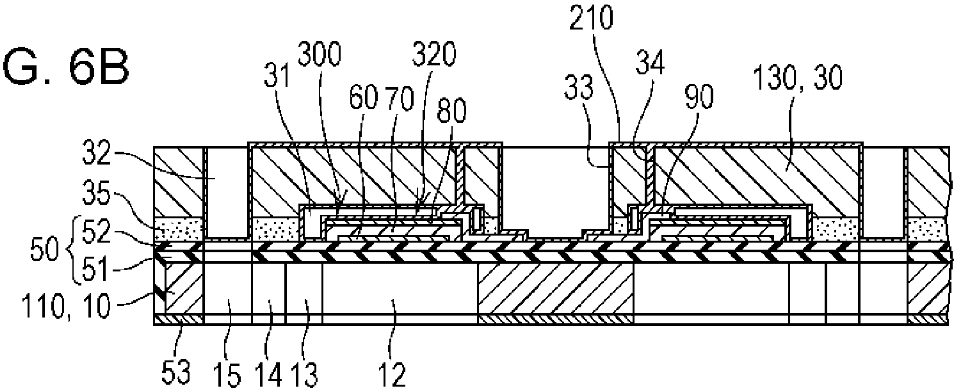
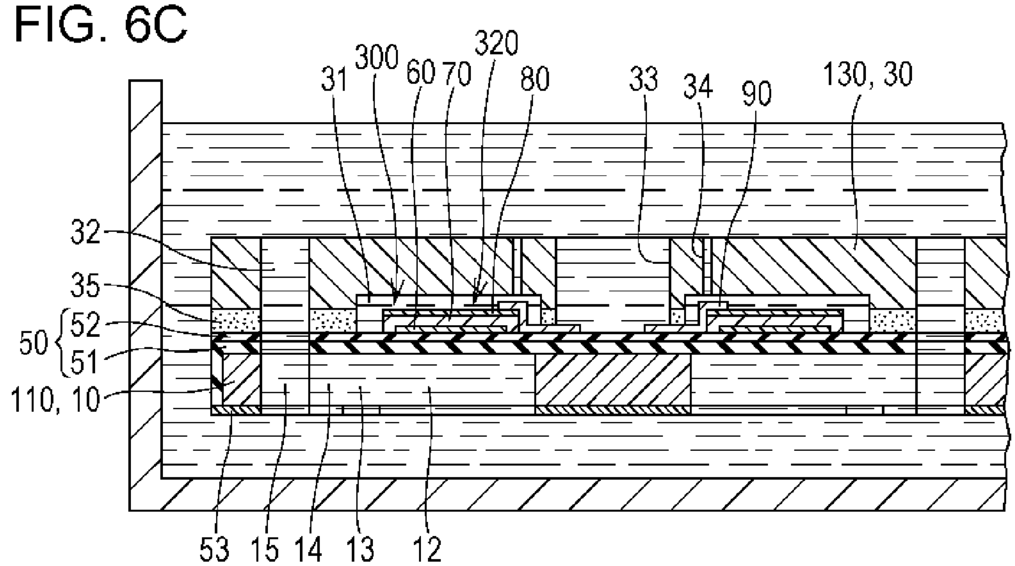


FIG. 6C



MANUFACTURING METHOD OF LIQUID EJECTING HEAD

BACKGROUND

1. Technical Field

The present invention relates to a manufacturing method of a liquid ejecting head which ejects liquid from nozzle openings, particularly a manufacturing method of an ink jet type recording head which discharges ink as liquid.

2. Related Art

There is a known ink jet type recording head which is the liquid ejecting head including a flow path formation substrate in which a pressure generation chamber communicating with nozzle openings is formed, a piezoelectric actuator which is provided on one surface side of the flow path formation substrate, and a protection substrate which is bonded to the flow path formation substrate on the piezoelectric actuator side.

In addition, such an ink jet type recording head is manufactured by forming the piezoelectric actuator on the flow path formation substrate which is formed of a silicon single-crystal substrate, then bonding the protection substrate to the upper portion thereof, and then, in a state where a surface of the protection substrate which is on the opposite surface side to the flow path formation substrate is covered and protected by a sealing sheet, performing wet etching of the flow path formation substrate with an etching solution formed of an alkaline aqueous solution such as KOH to form the pressure generation chamber and the like (for example, see Japanese Patent No. 4798348).

However, if the wet etching of the flow path formation substrate which is formed of a silicon single-crystal substrate is performed with the etching solution formed of an alkaline aqueous solution such as potassium hydroxide (KOH), hydrogen gas is generated and damages a piezoelectric layer so that a piezoelectric property of the piezoelectric layer is decreased.

Such a problem does not only occur in the manufacturing method of the ink jet type recording head, but also occurs in a manufacturing method of a liquid ejecting head which ejects liquid other than ink.

SUMMARY

An advantage of some aspects of the invention is to provide a manufacturing method of a liquid ejecting head in which damage to a piezoelectric element due to hydrogen is suppressed.

According to an aspect of the invention, there is provided a manufacturing method of a liquid ejecting head including a flow path formation substrate on which a pressure generation chamber communicating with nozzle openings for ejecting liquid is formed, a piezoelectric actuator which is provided on the flow path formation substrate, and a protection substrate which is bonded to the flow path formation substrate on the piezoelectric actuator side, the method including: bonding the flow path formation substrate on which the piezoelectric actuator is formed, and the protection substrate to form a bonded body; bonding a sealing member to the protection substrate of the bonded body on the surface side opposite the flow path formation substrate, and disposing a protection material containing a nitro compound in a space between the sealing member and the protection substrate; and performing wet etching of the flow path formation substrate of the bonded body to which the sealing member is bonded, to form the pressure generation chamber.

In this case, since hydrogen gas generated when performing the wet etching is adsorbed by the protection material containing the nitro compound, it is possible to suppress damage to the piezoelectric actuator due to the hydrogen gas.

Herein, it is preferable that, in the disposing of the protection material, the protection material be disposed at a temperature lower than a melting point thereof, and in performing the wet etching of the flow path formation substrate, the wet etching be performed at a temperature higher than the melting point of the protection material. According to this, since the protection material is solid when being disposed, it is possible to prevent a decrease of adhesiveness from occurring due to attachment of the protection material to a bonded surface of the sealing member or the like. In addition, since the protection material is liquid when performing the wet etching, hydrogen adsorption is efficiently performed.

In addition, it is preferable that the nitro compound contain at least one kind selected as a solvent from a group consisting of polyethylene glycol, polypropylene glycol, and polyglycerol. According to this, it is possible to easily set the protection film in a solid form at a normal temperature (room temperature) and in a liquid form at a temperature when performing the wet etching.

In addition, it is preferable that the flow path formation substrate be formed of a silicon substrate, and in performing wet etching of the flow path formation substrate, the wet etching be performed using potassium hydroxide. According to this, it is possible to form the pressure generation chamber or the like on the flow path formation substrate with high precision.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be described with reference to the accompanying drawings, wherein like numbers reference like elements.

FIG. **1** is an exploded perspective view of a recording head according to Embodiment 1 of the invention.

FIGS. **2**A and **2**B are a plan view and a cross-sectional view of a recording head according to Embodiment 1 of the invention.

FIGS. **3**A to **3**D are cross-sectional views showing a manufacturing method of a recording head according to Embodiment 1 of the invention.

FIGS. **4**A to **4**C are sectional views showing a manufacturing method of a recording head according to Embodiment 1 of the invention.

FIGS. **5**A and **5**B are sectional views showing a manufacturing method of a recording head according to Embodiment 1 of the invention.

FIGS. **6**A to **6**C are sectional views showing a manufacturing method of a recording head according to Embodiment 1 of the invention.

DESCRIPTION OF EXEMPLARY EMBODIMENTS

Hereinafter, the embodiment of the invention will be described in detail.

Embodiment 1

FIG. **1** is an exploded perspective view showing a schematic configuration of an ink jet type recording head which is an example of the liquid ejecting head according to Embodiment 1 of the invention and FIGS. **2**A and **2**B are a plan view of FIG. **1** and a cross-sectional view taken along line IIB-IIB, respectively.

As shown in the drawings, in the embodiment, a flow path formation substrate **10** included in an ink jet type recording head I which is an example of the liquid ejecting head of the embodiment is, for example, formed of a substrate including a silicon material, for example, a single-crystal silicon substrate or a polycrystal silicon substrate. In the flow path formation substrate **10**, pressure generation chambers **12** which are partitioned by a plurality of partition walls **11** are provided in a line along a direction in which a plurality of nozzle openings **21** ejecting ink are provided in a line. Hereinafter, this direction is referred to as a direction in which the pressure generation chambers **12** are provided in a line or a first direction X. In the embodiment, two columns of the pressure generation chamber **12** which are provided in a line along the first direction X, are provided along a second direction Y which intersects with the first direction X.

Ink supply paths **13** which apply flow path resistivity by setting an opening area of the pressure generation chamber **12** to be small, and communication paths **14** which have an opening area substantially the same as that of the pressure generation chamber **12** are divided by the plurality of partition walls **11** on one end portion side of the flow path formation substrate **10** in a longitudinal direction of the pressure generation chamber **12**, that is, on one end portion side in the second direction Y intersecting with the first direction X. A communication portion **15** configuring a part of a manifold **100** which is a common ink chamber (liquid chamber) of each pressure generation chamber **12** is formed on the outside of the communication path **14** (side opposite to the pressure generation chamber **12** in the second direction Y). That is, a liquid flow path formed of the pressure generation chamber **12**, the ink supply path **13**, the communication path **14**, and the communication portion **15** is provided on the flow path formation substrate **10**.

A nozzle plate **20** through which the nozzle openings **21** communicating with each pressure generation chamber **12** penetrate is bonded to one surface side of the flow path formation substrate **10**, that is, a surface on which the liquid flow path of the pressure generation chamber **12** or the like is opened, with an adhesive or a thermal welding film. In the embodiment, since the two columns in which the pressure generation chambers **12** are provided in a line in the first direction X, are provided in the second direction Y, two nozzle columns in which the nozzle openings **21** are provided in a line in the first direction X, are provided in the second direction Y, in one ink jet type recording head I.

A vibrating plate **50** is formed on the other surface side of the flow path formation substrate **10**. In the embodiment, the vibrating plate **50** is configured to include an elastic film **51** formed of silicon oxide which is provided on the flow path formation substrate **10** side and an insulating film **52** formed of zirconium oxide which is provided on the elastic film **51**. The liquid flow path such as the pressure generation chamber **12** is formed by performing anisotropic etching (wet etching) of the flow path formation substrate **10** from one surface thereof (a surface side to which a nozzle plate **20** is bonded), and the other surface of the liquid flow path such as the pressure generation chamber **12** or the like is partitioned by the elastic film **51**.

Herein, in addition to it being necessary that the vibrating plate **50** (in a case of laminated film, on electrode formation side) is an insulator and can withstand a temperature when forming the piezoelectric layer **70** (generally 500° C. or higher), in a case of using the anisotropic etching (wet etching) by KOH (potassium hydroxide) when forming a flow path such as the pressure generation chamber **12** using a silicon wafer for the flow path formation substrate **10**, it is necessary that the vibrating plate (in a laminated case, silicon wafer side) functions as an etching stopping layer. In addition, in a case of using silicon dioxide for a part of the vibrating plate **50**, if lead or bismuth contained in the piezoelectric layer **70** diffuses to silicon dioxide, silicon dioxide changes in properties and an electrode of an upper layer or the piezoelectric layer **70** is peeled off. Accordingly, a layer for preventing the diffusion thereof to silicon dioxide is also necessary.

Since each material of the vibrating plate **50** on which silicon dioxide and zirconium oxide are laminated, withstands the temperature when forming the piezoelectric layer **70**, silicon dioxide functions as an insulating layer and an etching stopping layer, and zirconium oxide functions as an insulating layer and a diffusion prevention layer, the vibrating plate **50** having this configuration is most preferable. In the embodiment, the vibrating plate **50** is formed with the elastic film **51** and the insulating film **52**, but either one of the elastic film **51** and the insulating film **52** may be provided as the vibrating plate **50**. In addition, a part of the flow path formation substrate **10** can be used as the vibrating plate by performing a thinning process.

In addition, a first electrode **60**, a piezoelectric layer **70**, and a second electrode **80** are formed by laminating by a process which will be described later to configure a piezoelectric actuator **300** on the insulating film **52** of the vibrating plate **50**. Herein, the piezoelectric actuator **300** is a portion including the first electrode **60**, the piezoelectric layer **70**, and the second electrode **80**. In general, any one electrode of the piezoelectric actuator **300** is set to a common electrode, and the other electrode and the piezoelectric layer **70** are patterned for each pressure generation chamber **12**. Herein, a portion which is configured from any one patterned electrode and the piezoelectric layer **70** and on which piezoelectric strain is generated by applying voltage to both electrodes is called a piezoelectric active portion **320**. In the embodiment, the first electrode **60** is set to a common electrode of the piezoelectric actuator **300** and the second electrode **80** is set to an individual electrode of the piezoelectric actuator **300**. However, there is no problem in the reverse case according to circumstances of a driving circuit or wiring. In the example described above, since the first electrode **60** is continuously provided over the plurality of pressure generation chambers **12**, the first electrode **60** functions as a part of the vibrating plate, but is not limited thereto, of course. For example, only the first electrode **60** may operate as the vibrating plate without providing the elastic film **51** and the insulating film **52**. In addition, the piezoelectric actuator **300** itself may substantially function as the vibrating plate. However, in a case of providing the first electrode **60** directly on the flow path formation substrate **10**, it is preferable to protect the first electrode **60** with an insulating protection film so that the first electrode **60** and the ink are not electrically connected to each other. That is, in the embodiment, the configuration in which the first electrode **60** is provided on the substrate (flow path formation substrate **10**) through the vibrating plate **50** is exemplified, but it is not particularly limited thereto, and the first electrode **60** may be directly provided on the substrate without providing the vibrating plate **50**. That is to say, the first electrode **60** may operate as the vibrating plate. That is, a phrase "on the substrate" includes a state directly on the substrate and a state with the other interposed member (upper portion).

In addition, the piezoelectric layer **70** is formed of a piezoelectric material such as oxide having a polarized structure which is formed on the first electrode **60**, and for example, can be formed of perovskite-type oxide shown as a general formula ABO_3. A can include lead, and B can include at least one of zirconium and titanium. B can further include niobium, for example. In detail, as the piezoelectric layer **70**, for example, lead zirconate titanate ($Pb(Zr,Ti)O_3$: PZT), or lead zirconate titanate niobate ($Pb(Zr,Ti,Nb)O_3$: PZTNS) containing silicon can be used.

The piezoelectric layer **70** may be set to composite oxide having a perovskite structure containing a lead-free piezoelectric material which does not contain lead such as bismuth ferrate or bismuth manganate ferrate, and barium titanate or bismuth potassium titanate.

In addition, a lead electrode **90** formed of, for example, gold (Au) which is extracted from the vicinity of the end portion which is on the side opposite the ink supply path **13** and is provided to extend to the upper portion of the vibrating plate **50**, is connected to each second electrode **80** which is an individual electrode of the piezoelectric actuator **300**.

A protection substrate **30** including a manifold portion **32** configuring at least a part of the manifold **100** is bonded to the upper portion of the flow path formation substrate **10** on which the piezoelectric actuator **300** is formed, that is, on the upper portions of the vibrating plate **50**, the first electrode **60**, and the lead electrode **90**, with an adhesive **35**. In the embodiment, the manifold portion **32** penetrates the protection substrate **30** in the thickness direction and is formed in the width direction of the pressure generation chamber **12**, and communicates with the communication portion **15** of the flow path formation substrate **10** as described above to configure the manifold **100** which is the common ink chamber of each pressure generation chamber **12**. In addition, the communication portion **15** of the flow path formation substrate **10** may be divided into plural portions for each pressure generation chamber **12**, and only the manifold portion **32** may be set as a manifold. Further, only the pressure generation chamber **12** may be provided on the flow path formation substrate **10**, and the ink supply path **13** communicating the manifold **100** and each pressure generation chamber **12** may be provided on the elastic film **51** and the insulating film **52** interposed between the flow path formation substrate **10** and the protection substrate **30**.

On the protection substrate **30**, a piezoelectric actuator holding portion **31** having a space for not inhibiting the driving of the piezoelectric actuator **300** is provided in a region facing the piezoelectric actuator **300**. The piezoelectric actuator holding portion **31** may have a space as long as it does not inhibit the driving of the piezoelectric actuator **300**, and the space may be sealed or not sealed. In the embodiment, an independent piezoelectric actuator holding portion **31** is formed for each column of the piezoelectric actuators **300** which are provided in a line in the first direction X. In addition, in the embodiment, an atmosphere release path **34** which communicates the piezoelectric actuator holding portion **31** and the outside is provided on the protection substrate **30**. Accordingly, by increasing pressure in the piezoelectric actuator holding portion **31** when the piezoelectric actuator **300** is deformed, it is possible to suppress inhibition of the deformation of the piezoelectric actuator **300**.

In addition, a penetration hole **33** which penetrates through the protection substrate **30** in the thickness direction is provided on the protection substrate **30**. The vicinity of the end portion of the lead electrode **90** which is extracted from each piezoelectric actuator **300** is provided so as to be exposed in the penetration hole **33**.

A driving circuit **120** which functions as a signal processing unit is fixed onto the protection substrate **30**. As the driving circuit **120**, a circuit board or a semiconductor integrated circuit (IC) can be used, for example. The driving circuit **120** and the lead electrode **90** are electrically connected to each other through a connection wire **121** formed of a conductive wire such as a bonding wire which is inserted through the penetration hole **33**.

As the protection substrate **30**, a material having substantially the same coefficient of thermal expansion as the flow path formation substrate **10**, for example, glass, a ceramic material, or the like is preferably used, and in the embodiment, a silicon single-crystal substrate which is made of the same material as that of the flow path formation substrate **10** is used for formation thereof.

A compliance substrate **40** formed of a sealing film **41** and a fixed plate **42** is bonded onto the protection substrate **30**. Herein, the sealing film **41** is formed of a flexible material having low rigidity, for example, polyphenylene sulfide (PPS) film, and one surface of the manifold portion **32** is sealed by the sealing film **41**. In addition, the fixed plate **42** is formed of a hard material such as metal, for example, stainless steel (SUS). Since the region of the fixed plate **42** facing the manifold **100** is set to an opening portion **43** which is completely removed in the thickness direction, one surface of the manifold **100** is sealed only with the sealing film **41** having flexibility.

In the ink jet type recording head I of the embodiment, the ink is introduced from an ink introduction port which is connected to an external ink supply unit (not shown), and the inside from the manifold **100** to the nozzle opening **21** is filled with the ink. After that, the piezoelectric actuator **300** corresponding to the pressure generation chamber **12** is driven according to a recording signal from the driving circuit **120**, and accordingly the vibrating plate **50** is bent and deformed. Therefore, the pressure in each pressure generation chamber **12** is increased, and ink droplets are discharged from the nozzle openings **21**.

Herein, a manufacturing method of the ink jet type recording head of the embodiment will be described with reference to FIGS. **3**A to **6**C. FIGS. **3**A to **6**C are cross-sectional views showing the manufacturing method of the ink jet type recording head according to the Embodiment 1 of the invention.

First, as shown in FIG. **3**A, the vibrating plate **50** is formed on a surface of a flow path formation substrate wafer **110** which is a silicon wafer. In the embodiment, the vibrating plate **50** which is formed of laminated layers of silicon dioxide (elastic film **51**) formed by thermal oxidation of the flow path formation substrate wafer **110** and zirconium oxide (insulating film **52**) formed by thermal oxidation after forming a film by a sputtering method, is formed.

In addition to it being necessary that the vibrating plate **50** (in a case of laminated film, on electrode formation side) is an insulator and can withstand the temperature when forming the piezoelectric layer **70** (generally 500° C. or higher), in a case of using the anisotropic etching by KOH (potassium hydroxide) when forming a flow path such as the pressure generation chamber **12** using a silicon wafer for the flow path formation substrate **10**, it is necessary that the vibrating plate (in a laminated case, silicon wafer side) functions as an etching stopping layer. In addition, in a case of using silicon dioxide for a part of the vibrating plate **50**, if lead or bismuth contained in the piezoelectric layer **70** diffuses to silicon dioxide, silicon dioxide changes in properties and an electrode of an upper layer or the piezoelectric layer **70** is peeled off. Accordingly, a layer for preventing the diffusion thereof to silicon dioxide is necessary.

Since each material of the vibrating plate **50** on which silicon dioxide and zirconium oxide are laminated, withstands the temperature when forming the piezoelectric layer **70**, silicon dioxide functions as an insulating layer and an etching stopping layer, and zirconium oxide functions as an insulating layer and a diffusion prevention layer, the vibrating plate **50** having this configuration is most preferable. In the embodiment, the vibrating plate **50** is formed with the elastic film **51** and the insulating film **52**, but either one of the elastic film **51** and the insulating film **52** may be provided as the vibrating plate **50**.

Next, as shown in FIG. **3**B, the first electrode **60** is formed on the entire surface of the vibrating plate **50** and is patterned in a predetermined shape. The material of the first electrode **60** is not particularly limited, but is necessarily a material which does not lose conductivity due to oxidation at the time of performing thermal treatment (generally 500° C. or higher) when forming the piezoelectric layer **70** or diffusion of the material contained in the piezoelectric layer **70**. Accordingly, metal such as platinum, iridium, or the like which does not lose conductivity even at a high temperature, or conductive oxide such as iridium oxide, lanthanum nickel oxide, or the like, and a layered material of the materials thereof are preferably used as the material of the first electrode **60**. In addition, the first electrode **60** can be formed, for example, with a vapor phase film by a sputtering method, a physical vapor deposition (PVD) method, a laser ablation method or the like, or a liquid phase film by a spin coating method. An adhesion layer for securing adhesiveness between the conductive material described above and the vibrating plate **50** may be used. In the embodiment, although not particularly shown in the drawings, titanium is used as the adhesion layer. As the adhesion layer, zirconium, titanium or titanium oxide can be used. A method of forming the adhesion layer is the same as that of the electrode material. In addition, a control layer for controlling crystal growth of the piezoelectric layer **70** may be formed on the electrode surface (film forming side of the piezoelectric layer **70**). In the embodiment, titanium is used for control of crystals of the piezoelectric layer **70** (PZT). Since the titanium is introduced into the piezoelectric layer **70** when forming the piezoelectric layer **70**, titanium does not exist as a film after forming the piezoelectric layer **70**. As the crystal control layer, conductive oxide having a perovskite-type crystal structure such as lanthanum nickel oxide may be used. A method of forming the crystal control layer is the same as that of the electrode material. The insulating crystal control layer desirably does not exist between the piezoelectric layer **70** and the first electrode **60** after forming the piezoelectric layer **70**. This is because the capacitors of the crystal control layer and the piezoelectric layer **70** are connected to each other in series, and therefore an electric field to be applied to the piezoelectric layer **70** is decreased. As the embodiment, by using titanium as an orientation control layer, the orientation control layer is introduced into the piezoelectric layer **70** and therefore does not exist as a film, while it is supposed to be subjected to the thermal treatment to become an oxide (insulator).

Next, as shown in FIG. **3**C, the piezoelectric layer **70** and the second electrode **80** are sequentially formed and laminated on the first electrode **60**. Herein, in the embodiment, the piezoelectric layer **70** is formed by using a so-called sol-gel method for obtaining the piezoelectric layer **70** formed of metal oxide by coating and drying a so-called sol which is obtained by dissolving and dispersing a metal complex in a solvent to be converted into a gel and burning the gel at a high temperature. The manufacturing method of the piezoelectric layer **70** is not limited to the sol-gel method, and for example, a metal-organic decomposition (MOD) method or the physical vapor deposition (PVD) such as the sputtering method or the laser ablation may be used. That is, the piezoelectric layer **70** may be formed by either the liquid phase method or the vapor phase method. In addition, metal having high conductivity, for example, iridium (Ir) or the like can be used for the second electrode **80**.

Next, as shown in FIG. **3**D, by patterning the piezoelectric layer **70** and the second electrode **80** at the same time, the piezoelectric actuator **300** is formed. For example, dry etching such as reactive ion etching or ion milling is used for the patterning of the piezoelectric layer **70** and the second electrode **80**.

Next, as shown in FIG. **4**A, the lead electrode **90** formed of gold (Au) is formed and is patterned in a predetermined shape.

Next, as shown in FIG. **4**B, after bonding a protection substrate wafer **130** which is a silicon wafer and is the plurality of protection substrates **30** to the piezoelectric actuator **300** side of the flow path formation substrate wafer **110** through the adhesive **35** to form a bonded body, the flow path formation substrate wafer **110** is set to be thinned to a predetermined thickness.

Next, as shown in FIG. **4**C, a mask film **53** is newly formed on the flow path formation substrate wafer **110** and is patterned in a predetermined shape.

Next, as shown in FIG. **5**A, a sealing member **200** is bonded to the surface of the protection substrate wafer **130** on the side opposite the surface to which the flow path formation substrate wafer **110** is bonded, through an adhesive **201**, and a protection material **210** containing a nitro compound is disposed between the sealing member **200** and the protection substrate wafer **130**.

Herein, the sealing member **200** has a sheet shape and covers the surface of the protection substrate wafer **130**, and accordingly the sealing member **200** seals the manifold portion **32** and the penetration hole **33** which is formed on the protection substrate wafer **130**.

At this time, the sealing member **200** is adhered to an periphery portion of the surface of the protection substrate wafer **130** through the adhesive **201** and is not adhered to a region which is separated to be the protection substrate **30** in a subsequent step.

The sealing member **200** is formed with a material having durability for an alkaline aqueous solution which is used when performing the wet etching of the flow path formation substrate wafer **110**. As the material of such a sealing member **200**, polyparaphenylene terephthalamide (PPTA) is used, for example. Although not particularly shown in the drawings, the sealing member **200** may include a protection sheet formed with a protection material, in a region which comes into contact with the protection substrate wafer **130**. Examples of the protection material include polytetrafluoroethylene (PTFE), polyethylene terephthalate (PET), polyphenylene sulfide (PPS), and the like. Particularly, a material which does not negatively affect the surface of the protection substrate wafer **130**, that is, a polymer material which does not interfere with the surface of the protection substrate wafer **130** is preferably used. As such a material, a fluorine resin or the like can be used, and in the embodiment, polytetrafluoroethylene (PTFE) is used.

In addition, the protection material **210** contains the nitro compound. If liquid is used as the protection material **210**, when bonding the sealing member **200** to the protection substrate wafer **130**, the liquid applies to the protection substrate wafer **130** or the sealing member **200**, but the applied liquid may be attached to the adhered surface due to a capillary phenomenon, adhesiveness between the protection substrate wafer **130** and the sealing member **200** may decrease, and accordingly, an etching solution may enter therebetween. Thus, the protection material **210** is preferably solid when being disposed between the protection substrate wafer **130** and the sealing member **200**.

In addition, the nitro compound contained in the protection material **210** is a hydrogen adsorbent which adsorbs hydrogen generated when performing the wet etching of the flow path formation substrate wafer **110**. Accordingly, when performing the wet etching of the flow path formation substrate wafer **110**, the protection material is preferably liquid to efficiently perform the adsorption of hydrogen. Therefore, the protection material **210** is preferably solid at a normal temperature and liquid at a temperature (approximately 80° C.) obtained by heating when performing the wet etching. That is, the protection material **210** is formed of a solid at a normal temperature, and in a step of performing the wet etching of the flow path formation substrate wafer **110**, the wet etching is preferably performed at a temperature (approximately 80° C.) which is higher than a melting point of the protection material **210**. Accordingly, when performing the wet etching of the flow path formation substrate wafer **110**, the protection material **210** is converted to a liquid and the inner portion of the manifold portion **32** and the penetration hole **33** can be filled with the nitro compound. As a solvent of the protection material **210** satisfying such conditions, polyethylene glycol, polypropylene glycol, polyglycerol, or the like is used, for example. That is, the protection material **210** includes at least one kind of solvent selected from a group consisting of polyethylene glycol, polypropylene glycol, and polyglycerol.

In the protection material **210**, the solvent of polyethylene glycol is heated to be converted to a liquid and the nitro compound is dissolved in this solvent. The obtained nitro compound solution is applied thereto and by returning the temperature to a normal temperature, the nitro compound solution can be formed in a sheet shape (solid). The protection material **210** including the nitro compound formed in a sheet shape can be easily disposed between the sealing member **200** and the protection substrate wafer **130**, and since the protection material **210** is solid, it is possible to suppress the attachment of the protection material **210** to the bonded surface of the sealing member **200** and the protection substrate wafer **130** due to the capillary phenomenon in order to suppress the decrease of adhesiveness.

As shown in FIG. **5**B, by performing anisotropic etching (wet etching) of the flow path formation substrate wafer **110** using the alkaline aqueous solution through the mask film **53**, the pressure generation chamber **12**, the ink supply path **13**, the communication path **14**, and the communication portion **15** corresponding to the piezoelectric actuator **300** are formed. In the embodiment, by immersing the bonded body of the protection substrate wafer **130** to which the sealing member **200** is bonded and the flow path formation substrate wafer **110** in KOH which is heated to approximately 80° C., the wet etching is performed.

Herein, as the alkaline aqueous solution used as the etching solution, potassium hydroxide (KOH), tetramethylammonium hydroxide (TMAH), sodium hydroxide (NaOH) or the like can be used, for example.

If the flow path formation substrate **10** including the silicon material (flow path formation substrate wafer **110**) is etched with the alkaline aqueous solution described above, silicon included in the flow path formation substrate **10** and a component included in the alkaline aqueous solution react with each other to generate hydrogen gas. Hereinafter, a reaction between the alkaline aqueous solution described above and the silicon is shown.

$$Si+2OH^-+4H_2$$

$$\rightarrow Si(OH)_2{}^{2+}4e^-+4H_2O$$

$$\rightarrow Si(OH)_2{}^{2+}+2H_2+4OH^-$$

$$\rightarrow Si(OH)_2{}^{2-}+2H_{2\uparrow}+2H_2O$$

As described above, the hydrogen gas generated when performing the wet etching of the flow path formation substrate wafer **110** using the alkaline aqueous solution has a small molecular weight, and accordingly enters the manifold portion **32** and the penetration hole **33** through boundaries of the adhesives **35** and **201**. The hydrogen gas which has entered the manifold portion **32** or the penetration hole **33** enters the piezoelectric actuator holding portion **31** by passing through the boundaries of the atmosphere release path **34** or the adhesive **35**, the entered hydrogen gas damages the piezoelectric layer **70**, and a piezoelectric property of the piezoelectric layer is degraded.

In the embodiment, by providing the protection material **210** including the nitro compound, between the protection substrate wafer **130** and the sealing member **200**, the protection material **210** adsorbs the hydrogen which has entered the inside thereof, and it is possible to suppress the hydrogen gas which has entered the piezoelectric actuator holding portion **31**. That is, the protection material **210** is preferably provided in the piezoelectric actuator holding portion **31** which is a space in which the piezoelectric actuator **300** is provided, or a space around this space, that is, in the manifold portion **32** and the penetration hole **33**. In the embodiment, the protection material **210** is provided between the protection substrate wafer **130** and the sealing member **200**, and since the protection material **210** becomes liquid by heating when performing the wet etching of the flow path formation substrate wafer **110** and is filled in the piezoelectric actuator holding portion **31** or in the manifold portion **32** and the penetration hole **33**, it is possible to efficiently adsorb hydrogen and to decrease damage to the piezoelectric layer **70** due to hydrogen.

Next, as shown in FIG. **6**A, the bonded body to which the sealing member **200** is bonded is extracted from the etching solution. Accordingly, the temperature of the bonded body returns to room temperature, and the protection material **210** which fills the manifold portion **32**, the piezoelectric actuator holding portion **31**, and the penetration hole **33** as liquid is attached to wall surfaces of the manifold portion **32**, the piezoelectric actuator holding portion **31**, and the penetration hole **33** in a solidified state.

Next, as shown in FIG. **6**B, the sealing member **200** is peeled off. For example, in a case where the sealing member **200** is adhered to a region of the protection substrate wafer **130** which is not the protection substrates **30** through the adhesive **201**, by cutting and removing an extra portion of the protection substrate wafer **130**, the sealing member **200** can be peeled off. That is, the step of peeling off the sealing member **200**, and the step of removing an unnecessary portion on an outer periphery portion of the flow path formation substrate wafer **110** and the protection substrate wafer **130** by cutting, for example, by dicing or the like, can be performed at the same time.

Next, as shown in FIG. **6**C, the bonded body of the flow path formation substrate wafer **110** and the protection substrate wafer **130** is cleaned. In the embodiment, cleaning is performed by immersing the bonded body in water. Since a solvent such as polyethylene glycol contained in the protection material **210** is water-soluble, by performing water cleaning, the protection material **210** which is solidified on the wall surfaces of the manifold portion **32**, the piezoelectric actuator holding portion **31**, and the penetration hole **33** is removed.

After that, the nozzle plate **20** through which the plurality of nozzle openings **21** are penetrated is bonded to the surface of the flow path formation substrate wafer **110** on the side opposite the protection substrate wafer **130**, the compliance substrate **40** is bonded to the protection substrate wafer **130**, and the flow path formation substrate wafer **110** and the like are divided into chip-sized flow path formation substrates **10** as shown in FIG. **1**, to obtain the ink jet type recording head of the embodiment.

As described above, in the embodiment, by performing the wet etching of the flow path formation substrate **10** (flow path formation substrate wafer **110**), the hydrogen gas generated when forming the pressure generation chamber **12** or the like is adsorbed by the protection material **210** including the nitro compound, and accordingly, it is possible to suppress the damage to the piezoelectric layer **70** due to hydrogen and to suppress the decrease of the piezoelectric property. Particularly, as the protection material **210**, by using a solvent which is solid at room temperature and is liquid at the temperature when performing the wet etching, it is possible to efficiently adsorb the hydrogen gas generated when performing the wet etching by the protection material **210** in a liquid form. In addition, by using the protection material **210** in a solid form, when disposing the protection material **210** between the sealing member **200** and the protection substrate **30** (protection substrate wafer **130**), it is possible to suppress attachment thereof to the adhered surface or the like and to suppress the decrease of the adhesiveness.

Other Embodiment

Hereinabove, one embodiment of the invention has been described. However the basic configuration of the invention is not limited thereto.

For example, in Embodiment 1 described above, the solvent which is solid at room temperature and is liquid at the temperature when performing the wet etching is used as the protection material **210**, but it is not particularly limited thereto, and the protection material **210** which is liquid at room temperature may be provided. In addition, the protection material **210** may be solid or may be in a powder form at room temperature.

In addition, in Embodiment 1 described above, the protection material **210** is removed by water cleaning, but it is not particularly limited thereto, and the protection material **210** may remain as it is, for example. Accordingly, since hydrogen contained in the atmosphere is adsorbed by the protection material **210**, it is possible to further suppress the damage to the piezoelectric layer **70** due to hydrogen during use.

Further, in Embodiment 1, the configuration of including the manifold portion **32** and the penetration hole **33** in the protection substrate **30** is exemplified, but it is not particularly limited thereto, and the manifold portion **32** or the penetration hole **33** may not be provided on the protection substrate **30**. It is only necessary to provide the protection material **210** in the piezoelectric actuator holding portion **31** of the protection substrate **30** or in the space in the vicinity thereof.

The invention is intended for a wide variety of general liquid ejecting heads, and can also be applied to manufacturing methods of a recording head such as various ink jet type recording heads used in an image recording apparatus such as a printer, a coloring material ejecting head used in manufacturing a color filter such as a liquid crystal display, an electrode material ejecting head used in electrode forming such as an organic EL display or a field emission display (FED), a bioorganic material ejecting head used in bio chip manufacturing, and the like.

The entire disclosure of Japanese Patent Application No. 2013-058559, filed Mar. 21, 2013 is expressly incorporated by reference herein.

What is claimed is:

1. A manufacturing method of a liquid ejecting head including a flow path formation substrate in which a pressure generation chamber communicating with a nozzle opening for ejecting liquid is formed, a piezoelectric actuator which is provided on the flow path formation substrate and associated with the pressure generation chamber, and a protection substrate which is bonded to the flow path formation substrate on the piezoelectric actuator side of the flow path formation substrate opposite the nozzle opening side, the method comprising:

bonding the flow path formation substrate on which the piezoelectric actuator is formed with the protection substrate to form a bonded body;

disposing a protection material containing a nitro compound on a surface side of the protection substrate that is opposite the flow path formation substrate;

bonding a sealing member to the protection substrate of the bonded body on a surface side opposite the flow path formation substrate such that the protection material is disposed in a space between the sealing member and the protection substrate; and

performing wet etching of the flow path formation substrate of the bonded body to which the sealing member is bonded to form the pressure generation chamber in the flow path formation substrate.

2. The manufacturing method of a liquid ejecting head according to claim **1**,

wherein disposing the protection material includes disposing the protection material a temperature lower than a melting point thereof, and

wherein performing includes performing wet etching at a temperature higher than a melting point of the protection material.

3. The manufacturing method of a liquid ejecting head according to claim **1**,

wherein the nitro compound contains at least one kind selected as a solvent from a group consisting of polyethylene glycol, polypropylene glycol, and polyglycerol.

4. The manufacturing method of a liquid ejecting head according to claim **1**,

wherein the flow path formation substrate is formed of a silicon substrate, and

wherein performing wet etching includes performing wet etching using potassium hydroxide.

* * * * *